

Principles of — Polymerization —

SECOND EDITION

George Odian

*Professor of Chemistry
The College of Staten Island
The City University of New York
Staten Island, New York*

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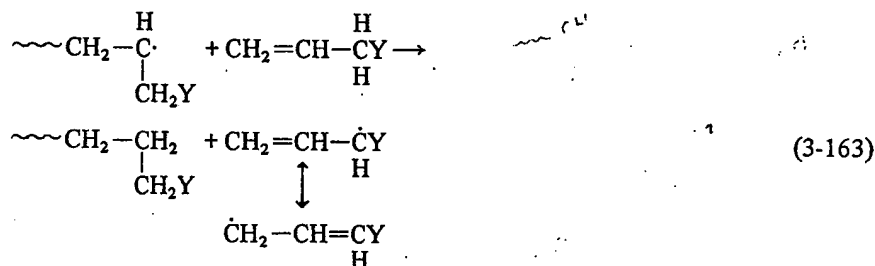
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oxygen [171]. Initiation probably occurs by thermal decomposition of the peroxides and hydroperoxides formed from the monomer (or, possibly more likely, from some impurity present in the system). Whether oxygen is an inhibitor or initiator will be highly temperature-dependent. Initiation will only occur at temperatures where the peroxides/hydroperoxides are unstable.

Other inhibitors include sulfur, carbon, aromatic azo compounds [172], and chlorophosphines [173].

3-7c Autoinhibition of Allylic Monomers

An especially interesting case of inhibition is the internal or *autoinhibition* of allylic monomers ($\text{CH}_2=\text{CH}-\text{CH}_2\text{Y}$). Allylic monomers such as allyl acetate polymerize at abnormally low rates with the unexpected dependence of the rate on the first power of the initiator concentration. Further, the degree of polymerization, which is independent of the polymerization rate, is very low—being only 14 for allyl acetate. These effects are the consequence of *degradative chain transfer* (Case 4 in Table 3-4). The propagating radical in such a polymerization is very reactive, while the allylic C—H (the C—H bond alpha to the double bond) in the monomer is quite weak—resulting in facile chain transfer to monomer



The weakness of the allylic C—H bond arises from the high resonance stability of the allylic radical which is formed. Degradative chain transfer competes exceptionally well with normal propagation and the polymer chains are terminated by transfer after the addition of only a very few monomer units. That the allylic C—H bond is the one broken in the transfer reaction has been shown [174] by experiments with $\text{CH}_2=\text{CH}-\text{CD}_2\text{OCOCH}_3$. The deuterated allyl acetate polymerizes 1.9–2.9 times as fast as normal allyl acetate and has a degree of polymerization 2.4 times as large under the same conditions. This is what would be expected since the C—D bond is stronger than the C—H bond due to its lower zero point energy and degradative chain transfer would therefore be decreased in the deuterated monomer.

The allylic radicals which are formed are too stable to initiate polymerization and the kinetic chain also terminates when the transfer occurs. The allylic radicals undergo termination by reaction with each other or, more likely, with propagating radicals [175]. Reaction 3-163 is equivalent to termination by an inhibitor, which is the monomer itself in this case. In this polymerization the propagation and termination reactions will have the same general kinetic expression with first-order

dependencies on initiator and monomer concentrations, since the same reactants and stoichiometry are involved. The degree of polymerization is simply the ratio of the rate constants for propagation and termination and is independent of the initiator concentration.

An alternate explanation is that allyl monomers are simply too low in reactivity to propagate extensively [176]. Data to support this mechanism are based on the low concentrations of allyl radicals observed by ESR relative to the concentrations of the propagating radicals. However, the overwhelming kinetic data support the degradative chain transfer mechanism.

The low reactivity of α -olefins such as propylene or of 1,1-dialkyl olefins such as isobutylene toward radical polymerization is probably a consequence of degradative chain transfer with the allylic hydrogens. It should be pointed out, however, that other monomers such as methyl methacrylate and methacrylonitrile, which also contain allylic C—H bonds, do not undergo extensive degradative chain transfer. This is due to the lowered reactivity of the propagating radicals in these monomers. The ester and nitrile substituents stabilize the radicals and decrease their reactivity toward transfer. Simultaneously the reactivity of the monomer toward propagation is enhanced. These monomers, unlike the α -olefins and 1,1-dialkyl olefins, yield high polymers in radical polymerizations.

3-8 DETERMINATION OF ABSOLUTE RATE CONSTANTS

3-8a Non-Steady-State Kinetics

There are five different types of rate constants that are of concern in radical chain polymerization—those for initiation, propagation, termination, chain transfer, and inhibition. The use of polymerization data under steady-state conditions allows the evaluation of only the initiation rate constant k_d (or k_i for thermal initiation). The ratio $k_p/k_t^{1/2}$ or k_p^2/k_t can be obtained from Eq. 3-25, since R_p , R_i , and $[M]$ are measurable. Similarly, the chain transfer constant k_{tr}/k_p and the inhibition constant k_z/k_p can be obtained by any of several methods discussed. However, steady-state data do not allow the evaluation of the individual k_p , k_t , k_{tr} , and k_z values. It is necessary to employ non-steady-state conditions to determine these individual rate constants. The treatment discussed here, for a photochemical polymerization, is essentially that of Flory [177] and Walling [133].

Radicals are generated abruptly by "putting on" the light source. The rates of initiation and termination are given by Eqs. 3-58 and 3-23, respectively. The rate of change of the radical concentration is given by the difference of their rates of production and termination

$$\frac{d[M\cdot]}{dt} = 2\phi I_a - 2k_t[M\cdot]^2 \quad (3-164)$$

For steady-state conditions $d[M\cdot]/dt$ is zero and

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